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Electron Diffraction Studies of Formaldehyde, Acetaldehyde and Acetone

Chuichi KATO,*[1] Shigehiro KONAKA, Takao IIJIMA and Masao KIMURA

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo

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The molecular structures of formaldehyde, acetaldehyde, and acetone have been investigated by the sector-microphotometer method of electron diffraction. Certain of the bonded interatomic distances, r_g, were determined to be as follows: for formaldehyde, $r(\text{C–O})=1.209_3\pm0.003_3$ Å and $r(\text{C–H})=1.096_7\pm0.053_5$ Å; for acetaldehyde, $r(\text{C=O})=1.208_5\pm0.003_3$ Å and $r(\text{C–C})=1.514_2\pm0.005_1$ Å; for acetone, $r(\text{C=O})=1.211_0\pm0.004_1$ Å and $r(\text{C–C})=1.516_7\pm0.004_8$ Å. The value of $r_g(\text{C=O})$ for formaldehyde was perfectly consistent wth the zero-point average distance, $r_z(\text{C=O})$, determined by microwave spectroscopy.

The structures of formaldehyde, acetaldehyde, and acetone have been the subject of a large number of structural investigations, for these compounds are the simple and elementary units of organic molecules containing carbonyl groups. Several structure determinations by microwave spectra have been published in the past decade.[1-3] In contrast to these studies by microwave spectra, however, studies by electron diffraction have so far been carried out[4-6] by the visual method and, necessarily, their results have included large uncertainties.

It is well known that bond lengths originally determined by microwave spectroscopy and by electron diffraction are not of the same physical siginificance, but can be related to each other by

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[*1] Present address: Fuji Iron and Steel Central Research Laboratory Co., Sagamihara, Japan.

1) HCHO: a) T. Oka, *J. Phys. Soc. Japan*, **15**, 2274 (1960); b) K. Takagi and T. Oka, *ibid.*, **18**, 1174 (1963).

2) CH_3CHO: a) R. W. Kilb, C. C. Lin and E. B. Wilson, Jr., *J. Chem. Phys.*, **26**, 1695 (1957); b) D. R. Herschbach, *ibid.*, **27**, 975 (1957).

3) $(CH_3)_2CO$: a) J. D. Swalen and C. C. Costain, *ibid.*, **31**, 1562 (1959); b) R. Nelson and L. Pierce, *J. Mol. Spectry.*, **18**, 344 (1965).

4) HCHO: D. P. Stevenson, J. E. LuValle and V. Schomaker, *J. Am. Chem. Soc.*, **61**, 2508 (1939).

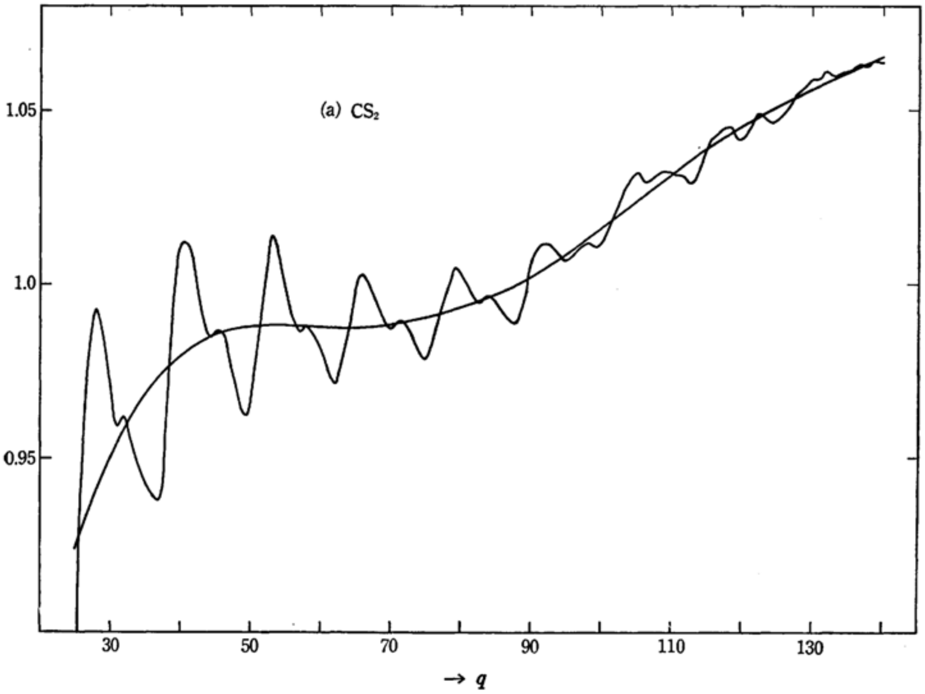
5) CH_3CHO: D. P. Stevenson, H. D. Burnham and V. Schomaker, *ibid.*, **61**, 2922 (1939); R. H. Schwendeman, *Diss. Abs.*, **18**, 1645 (1958).

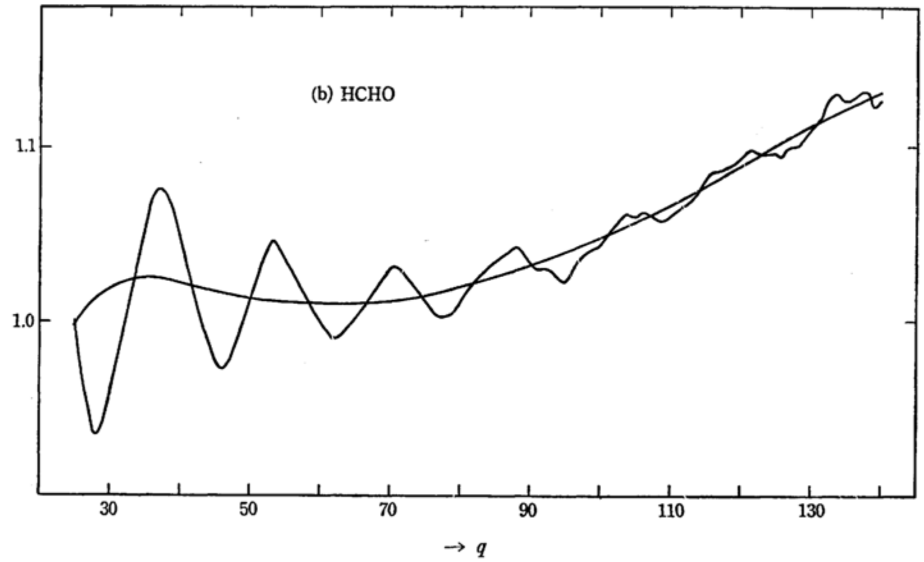
6) $(CH_3)_2CO$: O. Bastiansen and H. Viervoll, *Acta Chem. Scand.*, **2**, 702 (1948); M. Kimura and Y. Kurita, *Nippon Kagaku Zassi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **72**, 396 (1951); P. W. Allen, H. J. M. Bowen, L. E. Sutton and O. Bastiansen, *Trans. Faraday Soc.*, **48**, 991 (1952); C. Romers and J. E. G. Grentzberg, *Rec. Trav. Chim.*, **75**, 331 (1956).

taking into account the effect of thermal motions.[7] Since structure determinations for relatively complicated molecules must be performed on several assumptions when either method is used, microwave spectroscopy and electron diffraction may be considered to complement each other in determinations of molecular configurations.[8] Thus, the most reliable structures of formaldehyde, acetaldehyde, and acetone will be determined by combining information from electron diffraction with that from spectroscopy. The purpose of the present paper is to present the accurate molecular structures of these compounds as determined by the sector-microphotometer method of electron diffraction.

Experimental

The electron diffraction unit used in the present





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[7] Y. Morino, K. Kuchitsu and T. Oka, *J. Chem. Phys.*, **36**, 1108 (1962).

[8] K. Kuchitsu, T. Fukuyama and Y. Morino, *J. Mol. Structure*, **1**, 463 (1967—68).

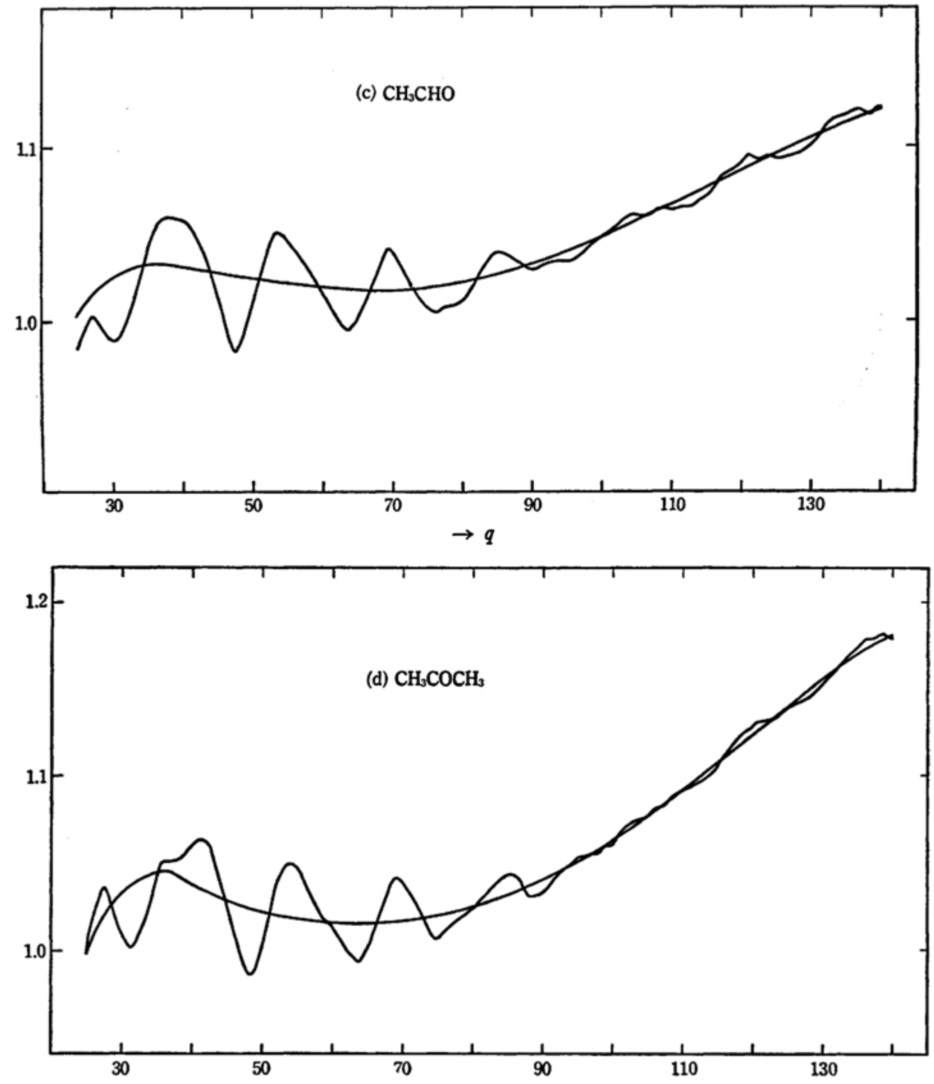
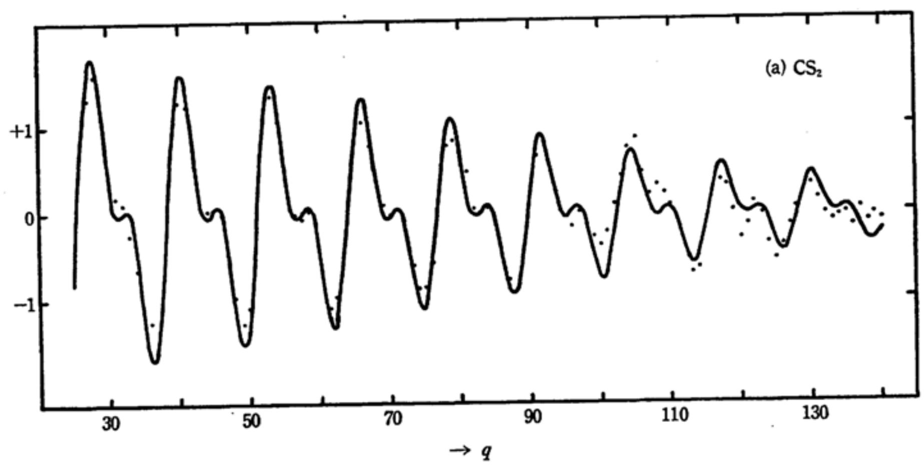


Fig. 1. Leveled intensities and backgrounds.
(a) CS_2, (b) HCHO, (c) CH_3CHO and (d) CH_3COCH_3.



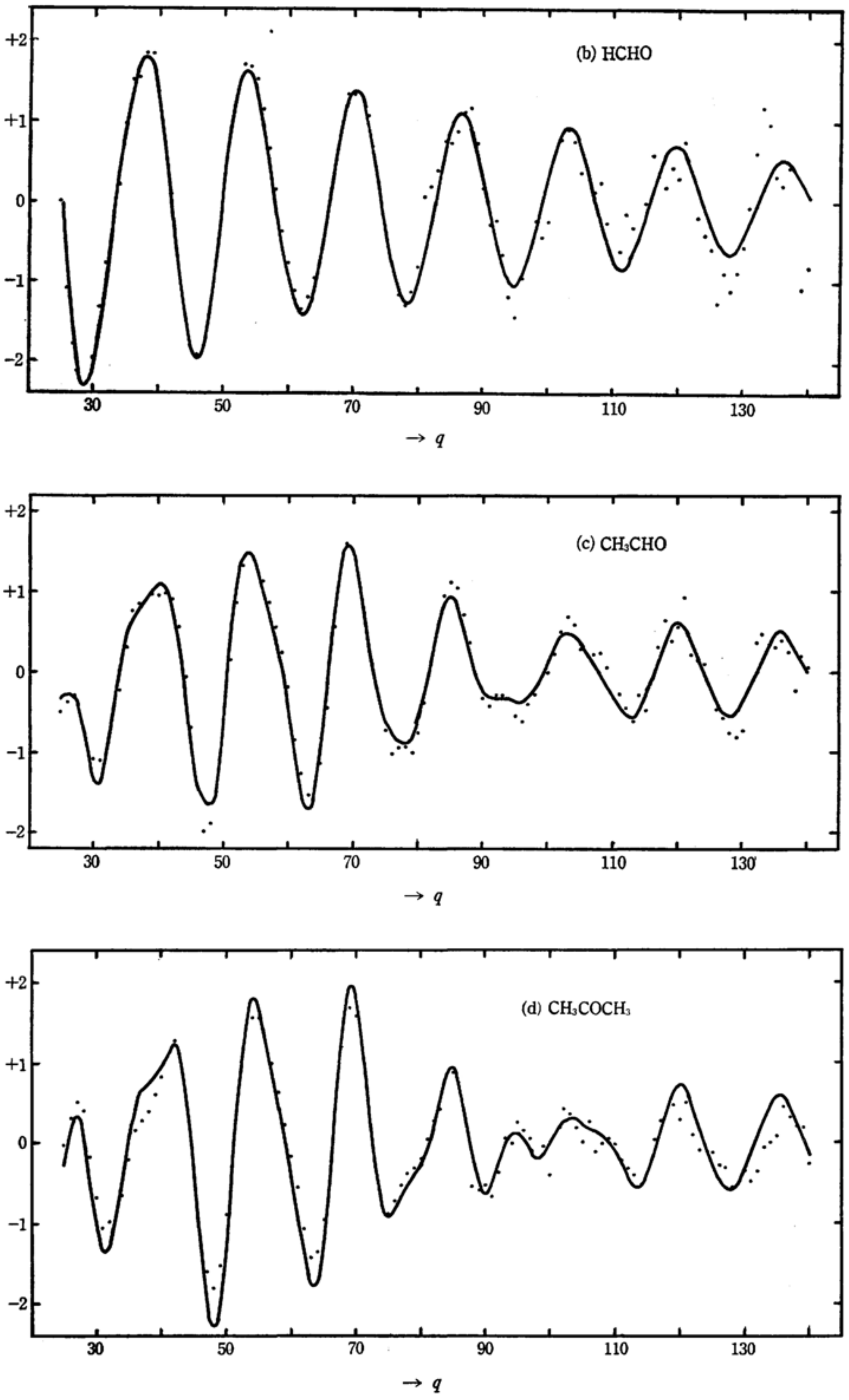
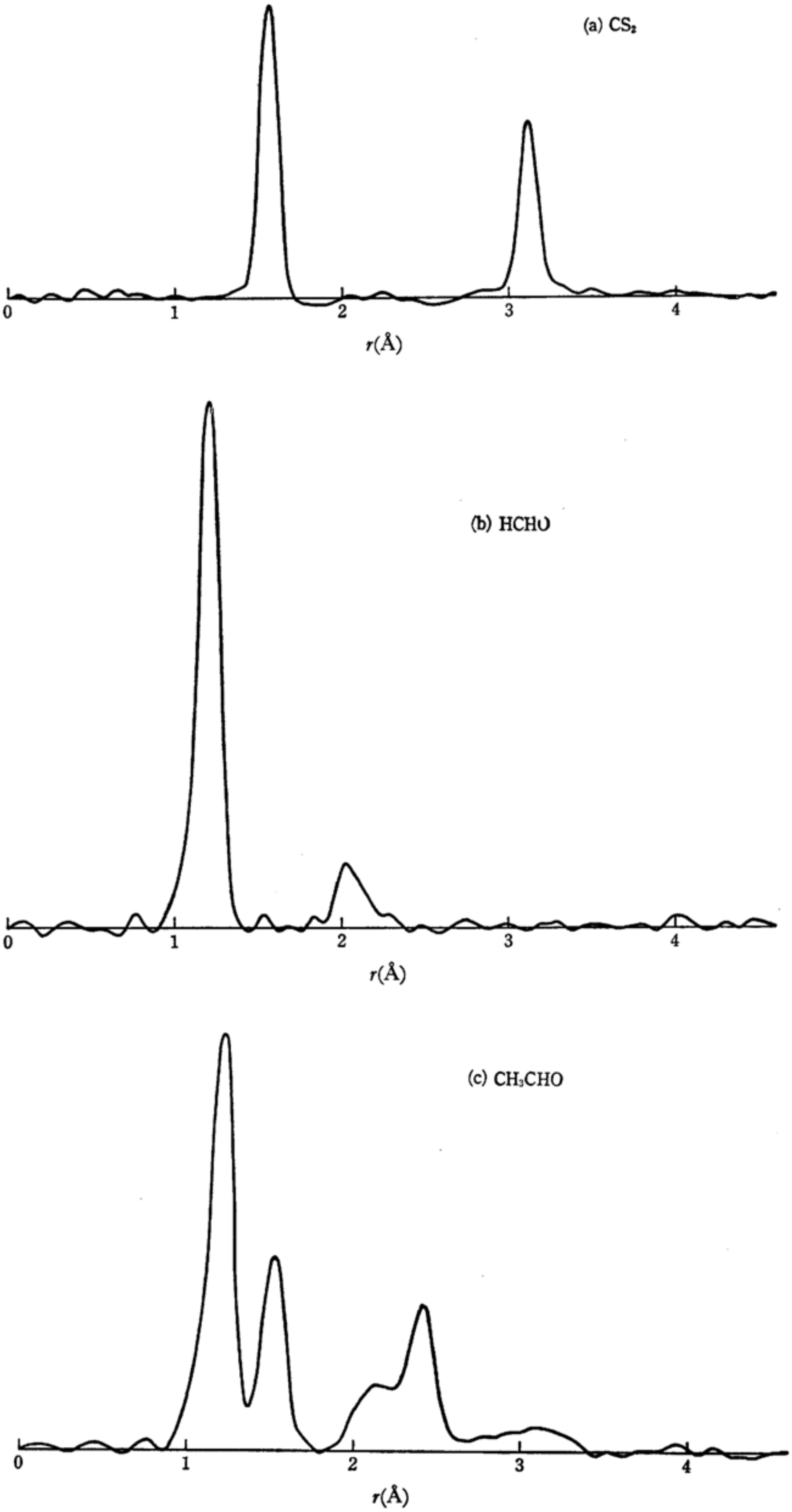


Fig. 2. Molecular intensity curves.
(a) CS_2, (b) HCHO, (c) CH_3CHO and (d) CH_3COCH_3.


(a) CS_2
0
1
2
3
4
r(Å)
(b) HCHO
0
1
2
3
4
r(Å)
(c) CH_3CHO
0
1
2
3
4
r(Å)

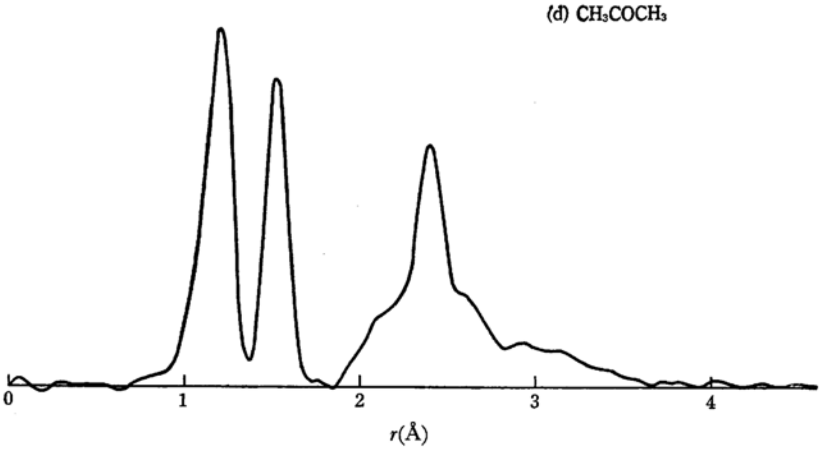


Fig. 3. Radical distribution curves.
(a) CS_2 (b) HCHO, (c) CH_3CHO and (d) CH_3COCH_3.

studies was newly designed and constructed. The camera lengths, the distance from the nozzle center to a plate, was perfectly fixed at 10.930 cm. Details about the unit will be reported elsewhere.[9] Diffraction photographs were taken with an r^3-sector at room temperature, 21.5°C. An accelerating voltage ($\sim$46 kV) was stabilized to within 0.1 percent throughout the sequence of exposures, which included a few pictures of the reference molecule and several pictures of sample molecules.

For the determinations of accelerating voltages, carbon disulfide was used as the reference material, for it has a suitable vapor pressure at room temperature and its distance parameters have been determined very accurately from spectroscopic data and confirmed by electron diffraction.[10] The use of a gaseous reference eliminates any systematic error due to the probable discrepancy between the nozzle and the actual diffraction centers and also some other systematic errors in the course of the experiment and analysis, for such errors are probably compensated for by employing the same procedure for both sample and reference gases.

The samples of carbon disulfide and acetone were special-grade reagents obtained from commercial sources. The sample of formaldehyde was prepared by the thermal depolymerization of commercial paraformaldehyde at 110°C according to the method of Spence and Wild.[11] Similarly, a sample of acetaldehyde was prepared by fractional distillation after depolymerizing commercial paraldehyde. The gases of carbon disulfide, formaldehyde, acetaldehyde, and acetone were stored in 1.5 *l* flasks at pressures of about 80 mmHg 120 mmHg, 135 mmHg, and 125 mmHg respectively, and then led into the diffraction chamber through a nozzle with an orifice 0.2 mm in diameter.

The photographic densities were measured by two different method: (1) with a double-beam microphotometer, model NLM-III, of the Narumi Co., Ltd, in our laboratory; this microphotometer was equipped with a cam converting transmission into optical density and a pen-recorder (pen-recording method), and (2) with a single-beam microphotometer, model MP-3, of the Rigaku Denki Co., Ltd., to which an integrating digital voltmeter was connected (digital method).[12],[*2] Measurements were made by scanning across the full diameters of the diffraction patterns while the photographic plates were being rotated about the diffraction centers. The diffraction intensities were determined by averaging the corresponding points on both sides of the center; they covered the range $q=25$—150 at intervals of $\Delta q=1.0$.

Analysis and Results

After correction for the deviation of the sector shape from an ideal r^3-curve, the measured total intensities were leveled by dividing by the smooth theoretical backgrounds. Examples of the leveled experimental intensities are shown in Fig. 1a—d. The backgrounds on these intensity curves (solid lines in Fig. 1) were not in perfect agreement with the theoretical values. Since photographs taken without the injection of gases were perfectly transparent, the turned-up backgrounds at larger scattering angles may be due mainly to the reflection of scattered electrons from the inside wall of the sector mount.[9] The final leveled intensities, I_T, were obtained by subtracting these extraneous backgrounds, which were assumed to be given by the deviations of the experimental backgrounds from the theoretical values normalized to the experimental values at $q=65$.

By drawing smooth backgrounds, I_B, through

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[9] Y. Murata, K. Kuchitsu and M. Kimura, *Japan. J. Appl. Phys.*, to be published.

[10] Y. Morino and T. Iijima, This Bulletin, **35**, 1661 (1962).

[11] R. Spence and W. Wild, *J. Chem. Soc.*, **1935**, 338.

[12] Y. Morino, K. Kuchitsu and T. Fukuyama, This Bulletin, **40**, 423 (1967).

[*2] The present authors wish to thank Professor Morino and his collaborators of the University of Tokyo for allowing us to use the microphotometer.

the leveled intensity curves, I_T, the molecular intensities, $qM(q)^{\mathrm{obs}}$, were obtained according to the equation:

$$qM(q)^{\mathrm{obs}} = q(I_T/I_B - 1) \tag{1}$$

The final smooth backgrounds and the corresponding molecular intensity curves were determined after Karle's criterion[13] by the Fourier inverse transformation of the radial distribution curves.[14] The molecular intensity curves and the radial distribution curves thus obtained are shown in Fig. 2a—d and Fig. 3a—d respectively.

The structure determinations were carried out by the method of least-squares applied to the molecular intensities, $qM(q)^{\mathrm{obs}}$, with a conventional weight function, as is shown in Fig. 4. The theoretical expression corresponding to the observed $qM(q)^{\mathrm{obs}}$ value is:

$$qM(q)^{\mathrm{calc}} = \kappa \sum_i {\sum_j}' A_{ij}\mu_{ij} \cos \Delta\eta_{ij}$$
$$\times \exp\left[-\frac{1}{2}\left(\frac{\pi}{10}q\right)^2 l^2{}_{ij}\right] \sin\left[\frac{\pi}{10}q\left\{r_{aij} - \left(\frac{\pi}{10}q\right)^2 \kappa_{ij}\right\}\right], \tag{2}$$

$$\left.\begin{aligned} A_{ij} &= \left(\frac{10}{\pi}\right)\frac{1}{r_{aij}} \cdot \frac{Z_iZ_j}{\sum_k Z_k(Z_k+1)}, \\ \mu_{ij} &= \frac{|F_i||F_j|}{\sum_k |F_k|^2 + \sum_k S_k} \cdot \frac{\sum_k Z_k(Z_k+1)}{Z_iZ_j}, \\ |F| &= (h^2s^2/8\pi^2 me^2)|f|, \; s = \frac{\pi}{10}\cdot q, \end{aligned}\right\} \tag{3}$$

where all the notations have their usual significances. The atomic scattering factors for electrons, $|f|$, and the phase shifts, $\Delta\eta_{ij}$, were those calculated by Kimura *et al.*,[15] while the inelastic scattering factors, S_k, were taken from the table given by Tavard *et al.*[16],*3 The starting models for the least-squares fittings are given in Table 1. Simultaneous least-squares refinements were not successful for all parameters because the low-weight

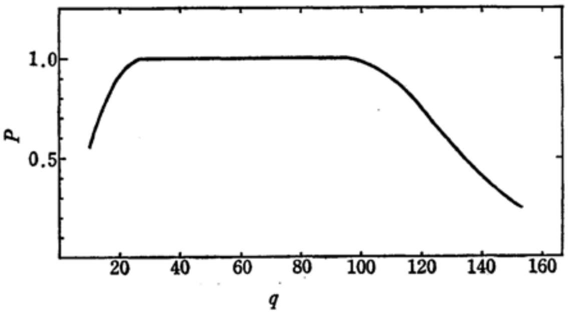

Fig. 4. Weight function.

TABLE 1.[a] MOLECULAR PARAMETERS CHOSEN AS THE STARTING MODELS FOR LEAST-SQUARES REFINEMENTS[b]

(a) CS_2: linear

	r_{ij}	l_{ij}	$\kappa_{ij}(\times 10^6)$
C-S	1.558	0.0391	(0.6)
S⋯S	3.109	0.0412	(0.5)

(b) HCHO: planar, C_{2v} symmetry

	r_{ij}	l_{ij}	$\kappa_{ij}(\times 10^6)$
C-O	1.208	0.0385	(0.7)
C-H	1.116	0.0802	(13.8)
O⋯H	2.032	0.0945	(8.8)

(c) CH_3CHO: C_s symmetry with the oxygen atom eclipsing a hydrogen atom of the CH_3 group.

	r_{ij}	l_{ij}	$\kappa_{ij}(\times 10^6)$
C-O	1.216	0.033	(0.4)
C⋯C	2.402	0.078	(4.1)
C-C	1.501	0.050	(2.1)
C-H(CH_3)	1.086	0.080	(13.7)
C-H	(1.114)	(0.080)	(13.7)
C⋯H(CH_3)	(2.142)	(0.098)	(10.2)
C⋯H(CHO)	(2.244)	(0.098)	(10.2)
O⋯H(CHO)	(2.004)	(0.091)	(7.6)
O:::H(CH_3)	(3.106)	(0.100)	(11.1)
O:::H(CH_3)	(2.707)	(0.100)	(11.1)

(d) CH_3COCH_3: C_{2v} symmetry with CH_3 groups eclipsed to a C=O bond.

	r_{ij}	l_{ij}	$\kappa_{ij}(\times 10^6)$
C-O	1.222	0.03	(0.3)
C⋯O	2.384	0.06	(1.4)
C-C	1.507	0.045	(1.4)
C⋯C	2.573	0.066	(2.1)
C-H	(1.085)	(0.077)	(11.7)
C⋯H	(2.145)	(0.100)	(11.1)
	(2.121)	(0.100)	(11.1)
C:::H	(2.863)	(0.11)	(16.3)
	(3.373)	(0.12)	(23.0)
O:::H	(3.067)	(0.100)	(11.1)
	(2.494)	(0.100)	(11.1)

a) Values associated with hydrogen-hydrogen pairs were dropped out from this table because of their very small contributions to molecular intensities.

b) In the least-squares treatment the values in parentheses were fixed, but the planarities of molecules were not assumed.

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[13] J. Karle and I. L. Karle, *J. Chem. Phys.*, **18**, 957 (1950); I. L. Karle and J. Karle, *ibid.*, **18**, 1963 (1950).

[14] R. A. Bonham and L. S. Bartell, *ibid.*, **31**, 702 (1959).

[15] M. Kimura, S. Konaka and M. Ogasawara, *ibid.*, **46**, 2599 (1967).

[16] C. Tavard, D. Nicolas and M. Rouault, *J. chim. phys.*, to be published.

*3 The authors wish to thank Dr. Tavard who kindly sent the complete table before publication.

structure parameters are very insensitive to refinement and, also, certain parameters are strongly correlated with one another. Assuming equal interatomic distances and mean amplitudes for the equivalent pairs of atoms, the parameters refined by the present least-squares treatments were as follows: for CS_2, k, r_a(C–S), r_a(S–S) and their associated mean amplitudes; for formaldehyde, k, r_a(C=O), r_a(O⋯H), r_a(C–H) and their associated mean amplitudes; for acetaldehyde, k, r_a(C=O), r_a(C–C), r_a(C⋯O), r_a(C–H methyl) and their associated mean amplitudes; and for acetone, k, r_a(C=O), r_a(C–C), r_a(C⋯O), r_a(C⋯C) and their associated mean amplitudes. The other parameters were all fixed at the assumed values indicated in parentheses in Table 1. The interatomic distances and mean amplitudes in Table 1 were selected from those given in previous structural studies of these molecules[1-6,10] and other related compounds. The anharmonicity constants, κ_{ij}, for carbon disulfide were given by Kuchitsu.[17] The values for bonded atom pairs of the other molecules were estimated from the following approximate equation:[18]

$$\kappa_{ij} \approx (1/9)l^2_{ij}\langle \Delta z_{ij}\rangle \approx (1/6)al^4_{ij} \tag{4}$$

assuming the Morse potentials with the asymmetry constant, a, of 2 Å^{-1}.[19] Although no proper method of estimating κ's is available for non-bonded atom pairs, it was suggested by Kuchitsu[17] that they appear several-fold smaller than the diatomic estimates given by Eq. (4). Therefore, the κ_{ij}'s for non-bonded atom pairs were assumed to be one-third of the values estimated from Eq.

TABLE 2. DETERMINATION OF A SCALE FACTOR BY THE USE OF THE STRUCTURE OF CARBON DISULFIDE

		Plate 1		Average	σ_1[b]	σ_2[b]	2.5σ[b]
		(I)	(II)				
k		0.938 ±0.026	0.860 ±0.030	0.899	0.020	0.039	0.095
r_a' (Å)[a]	C–S	1.5647±0.0011	1.5631±0.0013				
	S⋯S	3.1244±0.0020	3.1241±0.0022				
l_a (Å)	C–S	0.0371±0.0015	0.0374±0.0017	0.0373	0.0011	0.0002	0.0028
	S⋯S	0.0468±0.0020	0.0444±0.0022	0.0456	0.0015	0.0012	0.0038
$r_g'=r_a'+l_a^2/r_a'$ (Å)[a]	C–S	1.5657	1.5641	1.5649	0.0009	0.0008	
	S⋯S	3.1249	3.1247	3.1248	0.0014	0.0001	
s. f.[c]	C–S	0.99508±0.00069	0.99610±0.00083				
	S⋯S	0.99491±0.00063	0.99498±0.00070				
		0.99500	0.99554	0.99527			0.00207[d]
δ_g (Å)[e]		0.0065	0.0035	0.0050			

a) r_a' and r_g' denote the values obtained by presuming the camera length of 10.930 cm, and an accelerating voltage of 46 kV. b) See text.
c) Scale factor $= r_g/r_g'$, r_g(C–S)$=1.558$, r_g(S⋯S)$=3.109$, Ref. 10. d) See text. e) Shrinkage.

TABLE 3. RESULTS FOR FORMALDEHYDE

		Plate 1	Plate 2	Average	σ_1	σ_2	2.5σ
k		0.989 ±0.027	0.990 ±0.017	0.990	0.016	0.001	0.040
r_a (Å)	C–O	1.2137±0.0015	1.2113±0.0010				
	O⋯H	2.0534±0.0216	2.0596±0.0150				
	C–H	1.1186±0.0156	1.0679±0.0171				
$r_a+l_a^2/r_a$ (Å)	C–O	1.2149	1.2125				
	O⋯H	2.0577	2.0639				
	C–H	1.1232	1.0782				
s. f.		0.99527	0.99753				
r_g (Å)	C–O	1.2092	1.2095	1.2093	0.0009	0.0001	0.0022
	O⋯H	2.0480	2.0588	2.0534	0.0131	0.0054	0.0337
	C–H	1.1179	1.0755	1.0967	0.0117	0.0212	0.0530
l_a (Å)	C–O	0.0417±0.0019	0.0408±0.0012	0.0413	0.0011	0.0005	0.0037
	O⋯H	0.0898±0.0173	0.0932±0.0119	0.0915	0.0104	0.0017	0.0260
	C–H	0.0721±0.0130	0.1050±0.0094	0.0886	0.0080	0.0165	0.0413

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17) K. Kuchitsu, This Bulletin, **40**, 505 (1967).
18) Y. Morino and Y. Murata, *ibid.*, **38**, 104 (1965).
19) E. R. Lippincott and R. Schroeder, *J. Chem. Phys.*, **23**, 1131 (1955).

(4). At any rate, ambiguities in κ's have no substantial influence on the final results in the present studies.

The optical densities for each plate were measured by the two different methods described in the Experimental section. The least-squares refinements were applied to the individual molecular intensity curves. The results agreed with each other within their associated standard deviations, the interatomic distances especially being in perfect agreement. However, the standard deviations were smaller for the results obtained from optical densities by the digital method than for those obtained by the pen-recording method, for the former method gave the smoother intensity curves than the latter. Therefore, for the determinations of r_a and l_a we adopted only the results of the least-squares refinements applied to the whole range of observations by the digital method. The center of gravity of the probability function, r_g, can be obtained by the relation:

$$r_g = r_a + l_a^2/r_a. \qquad (5)$$

The scale factors for each sequence of exposures were determined by the use of the diffraction patterns of carbon disufide. Examples are shown in Table 2. Since the scale factors were very close to unity, no correction was made of parameters

TABLE 4. RESULTS FOR ACETALDEHYDE

		Plate 1	Plate 2	Average	σ_1	σ_2	2.5σ
k		1.008 ±0.034	0.992 ±0.035	1.000	0.035	0.008	0.088
r_a (Å)	C-O	1.2122±0.0012	1.2147±0.0012				
	C-C	1.5190±0.0026	1.5217±0.0028				
	C···O	2.4088±0.0043	2.4136±0.0043				
	C-H	1.1045±0.0093	1.0828±0.0089				
$r_a+l_a^2/r_a$ (Å)	C-O	1.2134	1.2159				
	C-C	1.5206	1.5233				
	C···O	2.4104	2.4150				
	C-H	1.1100	1.0884				
s. f.		0.99527	0.99452				
r_g (Å)	C-O	1.2077	1.2092	1.2085	0.0009	0.0008	0.0022
	C-C	1.5134	1.5150	1.5142	0.0016	0.0008	0.0040
	C···O	2.3990	2.4004	2.3997	0.0031	0.0007	0.0078
	C-H	1.0948	1.0769	1.0859	0.0091	0.0090	0.0228
l_a (Å)	C-O	0.0391±0.0015	0.0371±0.0016	0.0381	0.0011	0.0010	0.0028
	C-C	0.0492±0.0024	0.0502±0.0027	0.0497	0.0018	0.0005	0.0045
	C···O	0.0619±0.0036	0.0590±0.0036	0.0605	0.0025	0.0015	0.0064
	C-H	0.0862±0.0062	0.0839±0.0063	0.0851	0.0045	0.0012	0.0111

TABLE 5. RESULTS FOR ACETONE

		Plate 1	Plate 2	Average	σ_1	σ_2	2.5σ
k		0.930 ±0.028	0.930 ±0.030	0.930	0.021	0.000	0.051
r_a (Å)	C-O	1.2152±0.0017	1.2184±0.0021				
	C-C	1.5227±0.0018	1.5250±0.0023				
	C···O	2.3917±0.0031	2.3911±0.0039				
	C···C	2.6209±0.0128	2.6223±0.0141				
$r_a+l_a^2/r_a$ (Å)	C-O	1.2165	1.2197				
	C-C	1.5244	1.5267				
	C···O	2.3934	2.3927				
	C···C	2.6230	2.6244				
s. f.		0.99527	0.99309				
r_g (Å)	C-O	1.2107	1.2113	1.2110	0.0013	0.0003	0.0034
	C-C	1.5172	1.5162	1.5167	0.0015	0.0005	0.0038
	C···O	2.3821	2.3762	2.3792	0.0025	0.0030	0.0075
	C···C	2.6106	2.6063	2.6085	0.0095	0.0022	0.0237
l_a (Å)	C-O	0.0387±0.0017	0.0398±0.0021	0.0393	0.0013	0.0005	0.0034
	C-C	0.0495±0.0018	0.0487±0.0023	0.0491	0.0015	0.0004	0.0037
	C···O	0.0632±0.0026	0.0609±0.0033	0.0621	0.0021	0.0012	0.0053
	C···C	0.0750±0.0095	0.0739±0.0107	0.0745	0.0071	0.0005	0.0178

other than interatomic distances. The final values of r_g are given as averages of the r_g values determined separately for two selected plates. Tables 3, 4, and 5 show the results for formaldehyde, acetaldehyde, and acetone respectively.

The σ_1 and σ_2 values were estimated according to these two formulae: $\sigma_1^2 = \langle\sigma^2\rangle/2$ and $\sigma_2^2 = \sum v_i^2/n(n-1)$ respectively. Here, $\langle\sigma^2\rangle$ is the average of the square standard deviations for two plates, and v_i the residuals of the results of the ith plate subtracted from the average value. For most structure parameters, σ_2's were smaller than σ_1's. Taking the greater of σ_1 and σ_2 as a standard deviation, σ, for each parameter, random errors were given by 2.5 σ, representing 99% confidence intervals.

Five plates, one for each compound and two for carbon disulfide, were taken in a sequence of exposures; they are designated as plate 1 in the tables. Plate 2 for each compound was obtained in a separate sequence of exposures, one which included a plate for carbon disufide. The overall consistency in the results between plates 1 and 2 shows that the same experimental conditions were reproduced in the repeated exposures and that various systematic errors, such as errors originating from the drift of voltage, the uncertainty of the effective camera distance, *etc.*, may be regarded as being reflected in the error of the scale factor to be estimated below. Although a rigorous statistical meaning cannot be imposed on σ_2, which was estimated from only two plates in the present studies, σ_2 would coincide with σ_1 if a sufficiently large number of observations were made.

Since ach scale factor for plate 2 was determined by the analysis of only one plate of carbon disulfide, the largest standard deviation for individual scale factors may safely be taken as a standard deviation for all the scale factors used in the present studies. Thus, the error in the scale factor was given by 2.5 $\sigma = 0.00207$, and $\sigma = 0.00083$ for the C–S distance of plate 1 (II), corresponding to an error of 0.208 percent in interatomic distances. The total error for each parameter was considered to consist of two independent errors, the random error obtained in the least-squares fitting and the error in the scale factor. The final values of interatomic distances and their estimated total errors are given in Fig. 5. The interatomic distances obtained for acetone explain the planar frame of CCCO, as may clearly be seen by comparing them with the calculated values for a planar model shown in parentheses in Fig. 5.

The mean amplitudes, l_a, experimentally determined were not corrected for the effects of the sample size,[20] for the magnitudes of the corrections are much less than the total experimental errors. In Table 6 the final values of the mean amplitudes, l^{ED}, and their associated errors are summarized.

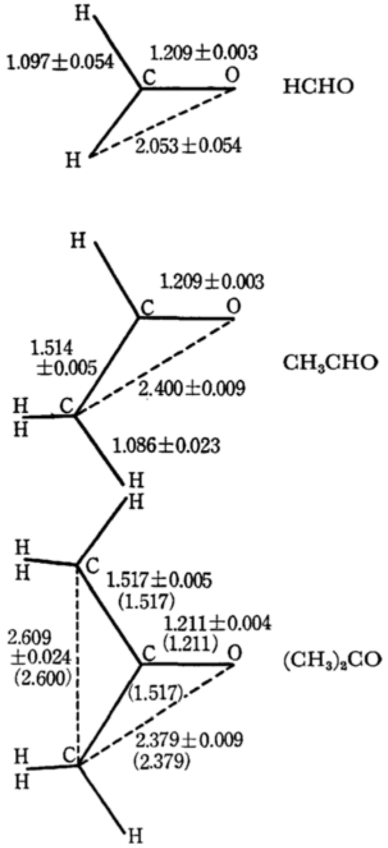

Fig. 5. The interatomic distances r_g in Å unit. The values in parentheses for acetone are interatomic distances calculated for a rigid model with the C_{2v} symmetry.

TABLE 6. MEAN AMPLITUDES OF FORMALDEHYDE, ACETALDEHYDE AND ACETONE AT 21.5°C

		$l^{ED\ a)}$	$l^{spectr\ b)}$
Formaldehyde	C–O	$0.041_3 \pm 0.004_0$	0.0385
	C–H	$0.088_6 \pm 0.041_3$	0.0802
	O···H	$0.091_5 \pm 0.036_5$	0.0945
Acetaldehyde	C–O	$0.038_1 \pm 0.004_0$	0.0389
	C–C	$0.049_7 \pm 0.006_5$	0.0493
	C–H	$0.085_1 \pm 0.015_8$	0.0778
	C···O	$0.060_5 \pm 0.009_0$	
Acetone	C–O	$0.039_3 \pm 0.004_8$	0.0399
	C–C	$0.049_1 \pm 0.005_3$	0.0513
	C···O	$0.062_1 \pm 0.007_5$	
	C···C	$0.074_5 \pm 0.025_3$	

a) The present study.
b) The fundamental frequencies and the set of force constants (VF. 3) of the valence force field in Ref. 22 were employed.

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[20] Y. Morino and Y. Murata, This Bulletin, **38**, 114 (1965).

TABLE 7. COMPARISON OF C=O AND C-C INTERATOMIC DISTANCES AS DETERMINED BY ELECTRON DIFFRACTION AND MICROWAVE SPECTROSCOPY

		C=O		C-C	
		ED	MW	ED	MW
HCHO	r_g	$1.209_3 \pm 0.003_3$	(1.2085)		
	r_z		$1.207_8 \pm 0.003$a)		
CH_3CHO	r_g	$1.208_5 \pm 0.003_3$		$1.514_2 \pm 0.005_1$	
	r_0		1.2155 ± 0.0020b)		1.501 ± 0.005b)
CH_3COCH_3	r_g	$1.211_0 \pm 0.004_1$		$1.516_7 \pm 0.004_8$	
	r_s		1.222 ± 0.003c)		1.507 ± 0.003c)

a) Ref. 1b. b) Ref. 2a. c) Ref. 3a.

Discussion

The results of the present studies show there is no significant difference in the carbon-oxygen bond lengths of formaldehyde, acetaldehyde, and acetone in spite of their different environments. In other words, the difference between H and CH_3 as substituents does not affect the carbon-oxygen bond lengths. The carbon-carbon bond lengths in acetaldehyde and acetone were almost the same, their values being intermediate between about 1.54 Å for single bonds and about 1.47 Å for central C–C single bonds in conjugated systems.

The mean amplitude, l_a, is approximately equal to the value of l_g, which refers to r_g, and also to l_α, which refers to the harmonic oscillators.17) Therefore, the observed values, l^{ED}, are in Table 6 compared with the values, l^{spectr}, calculated from the spectroscopic data, values which are equivalent to l_α. The l^{spectr} values were calculated by a usual method21) by the use of the fundamental frequencies and the force constants of the valence force field (the VF3 set) reported by Cossee and Schachtschneider.22) The agreements between l^{ED} and l^{spectr} are quite satisfactory.

Table 7 compares the bond lengths determined in the present study with those obtained from the rotational constants by microwave spectroscopy. For acetaldehyde and acetone, it is at this moment a question whether the bond lengths as determined by two different methods can be regarded as consistent with each other, for r_g, r_0, and r_s represent bond lengths with different physical significances.

Fortunately, the zero-point structure, r_z, for formaldehyde was given by Takagi and Oka.1b) Since the conversion of r_z into r_g can be made rather straightforwardly, r_g was estimated from the r_z for the C=O bond of formaldehyde. To a good approximation, r_z can be related to r_g by the equation:17,23)

$$r_g = r_z + \delta r + \frac{3}{2}a(l_T^2 - l_0^2) + [\langle \Delta x^2 \rangle_0 + \langle \Delta y^2 \rangle_0]/2r_a \tag{6}$$

Here, δr is the correction for the centrifugal distortion, $\langle \Delta x^2 \rangle_0$ and $\langle \Delta y^2 \rangle_0$ are the perpendicular mean amplitudes at 0°K, and l_T and l_0 are the parallel mean amplitudes at T °K and 0°K respectively. The values of $\langle \Delta x^2 \rangle$, $\langle \Delta y^2 \rangle$, and l_0 were calculated simultaneously in the calculations of l^{spectr}.21,24) The estimation of δr was based upon a model in which the CH_2 group and the oxygen atom were bound with a force constant of 11 md/Å (K(C=O) in Ref. 22) at a distance of 1.2078 Å (r_z in Ref. 1b). The numerical values thus calculated were 0.00062 Å for δr, 0.00000 Å for $(3/2)a(l_T^2 - l_0^2)$ and 0.00004 Å for $[\langle \Delta x^2 \rangle_0 + \langle \Delta y^2 \rangle_0]/2r_a$. The value of r_g estimated from r_z then becomes 1.2085 Å, which agrees almost perfectly with the r_g value obtained by electron diffraction.

It has recently been shown that a cooperative use of diffraction and spectroscopic data is most useful in obtaining accurate structures of medium-sized molecules.8) The present results for acetaldehyde and acetone must, therefore, be effectively combined with available spectroscopic informations. The application of this procedure to the structural studies of these molecules will be reported in separate papers.

The calculations of the least-squares analysis were carried out on the electronic computer, HITAC 5020 E, in the computing center of the University of Tokyo, to which the present authors' thanks are due.

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21) Y. Morino, K. Kuchitsu and T. Shimanouchi, *J. Chem. Phys.*, **20**, 726 (1952).

22) P. Cossee and J. H. Schachtschneider, *ibid.*, **44**, 97 (1966).

23) Y. Morino, K. Kuchitsu and T. Oka, *ibid.*, **36**, 1108 (1962).

24) Y. Morino and E. Hirota, *ibid.*, **23**, 737 (1955).